

## Insights into copper isotope fractionation during the oxidative phase transition of chalcocite, using time-resolved synchrotron X-Ray diffraction

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The focus of this research is to understand Cu isotope fractionation associated with the oxidative dissolution of secondary copper minerals. As previously shown, chalcocite (Cu<sub>2</sub>S) transforms to covellite (CuS) with a series of intermediate phases by the oxidation of Cu<sup>1+</sup> to Cu<sup>2+</sup> and the loss of Cu from the mineral structure. Mathur *et al.* (2005) have demonstrated that the Cu isotope composition of the solids becomes lighter during this reaction. In this study, we have combined time-resolved X-ray diffraction with Cu isotope measurements to monitor changes to Cu-S mineral structures and the concomitant isotopic fractionation of Cu.

Pure, naturally occurring chalcocite powders were placed in flow-through capillary reaction cells and exposed to various concentrations of aqueous ferric sulfate for up to 2 hrs. Real-time diffraction data were collected at intervals of 2 min at beam line X7B, National Synchrotron Light Source, using a MAR345 imaging plate. The  $\delta^{65}\text{Cu}$  values of the leached Cu as well as the starting and final powders were measured using a Finnigan Neptune multi-collector inductively coupled plasma mass spectrometer.

The powder diffraction data revealed that chalcocite passes through a complex series of partially oxidized intermediate phases during its transformation to covellite using 10<sup>-2</sup> M ferric sulfate. The untreated chalcocite powder had a  $\delta^{65}\text{Cu}$  value of 0.46±0.12‰ and the residual covellite had a  $\delta^{65}\text{Cu}$  value of 0.13±0.12‰. The  $\delta^{65}\text{Cu}$  value of the leachate sampled after 10 min. was 2.46±0.12‰. During the reaction  $\delta^{65}\text{Cu}$  values of the leachate decreased over time. The final leachate sample had  $\delta^{65}\text{Cu}$  values of -2.55±0.12‰. The most significant decrease in  $\delta^{65}\text{Cu}$  values of the leachate occurred during the transition of chalcocite to anilite and corresponded to the period of highest copper yield.

### References

Mathur R., Ruiz R., Titley S., Liermann L., Buss H. and Brantley S. (2005), *Geochim. Cosmochim. Acta.* **69** 5233-5246.

## Towards an understanding of biosilicification mechanisms: Nucleation of amorphous silica on organic surfaces

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Biochemical investigations have begun to yield information about structural and chemical properties of organic macromolecules involved in biosilicification processes. However, the mechanisms by which these molecules mediate biosilica formation remain unclear. Insights into how mineral formation occurs within living organisms can be gained by conducting experimental studies with simple model systems that emulate key features of biological systems. We employ a novel AFM-based approach to measure the dependence of amorphous silica nucleation kinetics on the chemical and structural nature of the underlying substrate.

The rate of silica nucleation was measured on COOH and mixed COOH/NH<sub>3</sub><sup>+</sup> surfaces, under conditions that simulate current views of the chemical environment within silica deposition vesicles of major diatom species (ambient temperature, pH = 5.0, NaCl = 0.1 mol/kg). Markedly faster rates were measured on mixed COOH/NH<sub>3</sub><sup>+</sup> surfaces than on either of the end-member films, suggesting that these two functional groups work in concert to promote the formation of silica at these interfaces. Differences between substrate-specific nucleation rates were determined to be controlled largely by kinetic factors rather than thermodynamic drivers. Further experiments with micro-patterned COOH and NH<sub>3</sub><sup>+</sup>-terminated surfaces also showed that the initial stage of silica deposition occurred at the COOH/NH<sub>3</sub><sup>+</sup> interface. Although silica nucleation was not initially observed on purely aminated surfaces, the introduction of orthophosphate triggered the deposition of silica on these surfaces as well.

These results give insight into how silica mineralization may be controlled by organisms like diatoms. Molecules that have been identified as part of the silicification mechanism either possess regions of locally concentrated positive and negative charge (silaffins), or require the presence of specific counterions such as phosphate to control silica deposition (polyamines). Phosphate anion has been previously implicated as having a probable role in controlling the self-assembly of these macromolecules into a template for silica deposition. Sites on the organic matrix that have phosphate and amine moieties in close proximity are likely to be points of initial silica deposition. These sites are also probable contact points between the constituent macromolecules in the matrix; hence, deposition of silica in these locations likely serves to cement the molecular elements of the organic matrix together.